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PATENT SPECIFICATION

NO DRAWINGS

Inventor: HARRY WESLEY COOVER, Jr.

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COMPLETE SPECIFICATION

Improved Graft Polymers

We, KODAK LIMITED, a Company registered under the Laws of Great Britain, of Kodak House, Kingsway, London, W.C.2 (Assignees of HARRY WESLEY COOVER, JR.), do hereby declare the invention (Communicated by Eastman Kodak Company, a Company organised under the laws of the State of New Jersey, United States of America, of 343, State Street, Rochester, New York, United States of America), for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

15 This invention relates to graft polymers, processes for the production of graft polymers and products manufactured therefrom.

It has been known that both vinyl chloride and vinylidene chloride give rise to polymers noted for their high softening temperature and excellent mechanical properties. However, it is also known that polymers of vinyl chloride and vinylidene chloride possess the undesirable property of lacking dye affinity.

25 Attempts have been made to increase the dyeability of vinyl chloride and vinylidene chloride fibres by interpolymerizing vinyl chloride or vinylidene chloride with certain monomers whose polymers have an affinity for dyes. While this procedure does give polymer products from which fibres having good dyeing properties can be obtained, a serious drawback frequently occurs a substantial lowering of the softening point of the fibre being observed.

Other attempts have been made to increase the dyeability of polyvinylidene chloride or polyvinyl chloride fibres by mixing them, before spinning, with other polymeric materials which are dye-susceptible. This procedure, likewise, provides fibres having good dyeing properties. However, many of these fibres show a low softening temperature and, in addition, many show segmentation into their individual

components along their horizontal axis. For example, it can be demonstrated that mixtures of polyvinyl acetate and polyvinyl chloride, when dissolved in either N,N-dimethylformamide or N,N-dimethylacetamide in proportions varying from 15 to 50% of polyvinyl acetate, based on the total weight of the mixed polyvinyl acetate and polyvinyl chloride, form grainy dopes which separate into two liquid layers on standing. This is also true of many other polymeric materials, natural or synthetic, which are soluble in the above solvents. Fibres which form from these non-homogeneous solutions or mixtures are too low in softening temperature to be of practical value and are also subject to the defect of segmentation. This is not surprising because of the non-homogeneous condition of the spinning solution and the fact generally known that polyvinyl chloride, or polyvinylidene chloride, is not compatible with many organic substances.

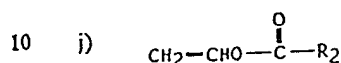
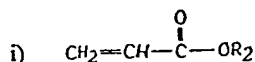
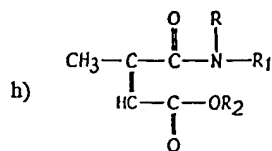
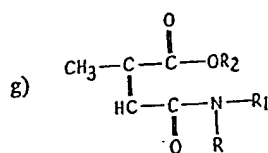
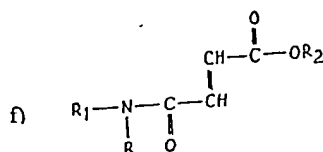
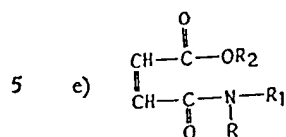
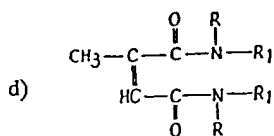
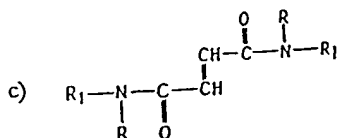
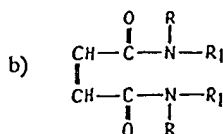
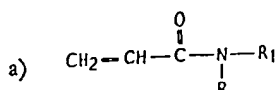
We have discovered new graft polymers and we have found that at least some of these graft polymers have valuable properties, particularly as regards their dyeability and their ability to form stable solutions from which, for example, fibres may be spun.

According to the present invention there is provided a process for preparing a graft polymer which comprises polymerising in a liquid medium from 95% to 5% by weight of monomer composition (1) containing from 30% to 100% by weight of vinyl chloride or vinylidene chloride or a mixture of said chlorides and from 70% to 0% by weight of a different, monoethylenically unsaturated, polymerisable compound containing a $-\text{CH}=\text{C}-$ group with from 5% to 95% by weight of a polymer formed by polymerisation of a monomer composition (2) containing from 1% to 100% by weight of a monomer represented by the following general formulas:

[Price 3s. 6d.]

Price 4s. 6d.

ATTORNEY DOCKET NUMBER: 9584-039-999
SERIAL NUMBER: 10/629,524
REFERENCE: B05



wherein R and R₁ each represents H or an alkyl group of from 1 to 6 carbon atoms and R₂ represents an alkyl group of from 1 to 4 carbon atoms, and from 99% to 0% by weight of a different, monoethylenically unsaturated, polymerisable compound containing a $-\text{CH}=\text{C}-$ group and which has or has not been isolated from its polymerisation medium, said percentages by weight of monomer compositions (1) and (2) being based on the total weight of these compositions (1) and (2).

In the process of the present invention composition (1) is polymerised in the presence of a polymer which is formed by the polymerisation of monomer composition (2). In one embodiment of this process, the first formed polymer is not isolated from the medium in which it is formed and in another embodiment the polymer is isolated from its polymerisation medium before composition (1) is polymerised therewith.

When the preformed polymer is separated from its polymerisation medium and redissolved in a solvent or suspended in an aqueous medium all of the reactive groups in the polymer chain are apparently closed or rendered inactive and polymerization of additional monomer with this separated polymer causes lowering of softening temperature in certain instances. Other properties of the polymer thus produced are also different. When the polymerisation is carried out in the presence of a polymer which has not been separated from its polymerisation medium the polymerisation of the added monomer, or monomers, proceeds by addition to unreacted portions of the reactive polymer, as well as undergoing some homo-polymerisation or inter-polymerisation.

Since the present invention relates both to the preparation of graft polymers of vinyl chloride and vinylidene chloride, for the sake of convenience, these monomers are hereinafter referred to as the chloride monomers. The polymers are similarly referred to.

The preformed polymers which are useful in imparting dye affinity to the vinyl chloride or vinylidene chloride polymers of the present invention comprise homopolymers and inter-polymers of the acrylamides, maleamides, fumaramides, citraconamides, maleamates, fumaramates, citraconamates, acrylates and vinyl esters. The acrylamides have been found especially useful when used according to the present invention.

The acrylamides which can be used in the present invention are those represented by the general formula a) as defined above. The alkyl groups which R and R₁ may each represent include methyl, ethyl, propyl, isopropyl, butyl and isobutyl. Typical acrylamides include, for example, acrylamide, N-methyl acrylamide, N-ethyl acrylamide, N-iso-propyl acrylamide, N-n-butyl acrylamide, N,N-dimethyl acryl-

amide, N,N-diethyl acrylamide. N-cyclohexyl acrylamides can also be used.

The maleamides which can be used are those represented by the general formula b) as defined above. Typical maleamides include, for example, maleamide, N-methylmaleamide, N-ethylmaleamide, N-propylmaleamide, N-isopropylmaleamide, N-n-butylmaleamide, N,N'-dimethylmaleamide, N,N'-diethylmaleamide, N,N'-di-n-butylmaleamide, N,N'-methylethylmaleamide, N,N'-tetramethylmaleamide, N,N'-tetraethylmaleamide and N,N'-dimethyl-N,N'-diethylmaleamide.

The fumaramides which can be used are those represented by the general formula c) as defined above. Typical fumaramides include, for example, fumaramide, N-methylfumaramide, N-ethylfumaramide, N-propylfumaramide, N-isopropylfumaramide, N-n-butylfumaramide, N,N'-dimethylfumaramide, N,N'-diethylfumaramide, N,N'-di-n-butylfumaramide, N-ethyl-N'-methylfumaramide, N-n-butyl-N'-methylfumaramide, N,N'-tetramethylfumaramide, N,N'-tetraethylfumaramide and N,N'-diethyl-N,N'-dimethylfumaramide.

The citraconamides which can be used are those represented by the general formula d) as defined above. Typical citraconamides include, for example, citraconamide, N-methylcitraconamide, N-ethylcitraconamide, N-n-butylcitraconamide, N,N'-dimethylcitraconamide, N,N'-diethylcitraconamide, the N,N'-butylcitraconamides and N,N'-tetramethylcitraconamide.

The maleamates which can be used are those represented by the general formula e) as defined above. The alkyl groups which R₁ represents include methyl, ethyl, propyl, isopropyl, n-butyl and isobutyl. Typical maleamates are methyl maleamate, propyl maleamate, N-methyl methyl maleamate, N-ethyl methyl maleamate, the N-butyl methyl maleamates, the N-methyl butyl maleamates, N-dimethyl methyl maleamate, N-dimethyl ethyl maleamate, N-dimethyl n-butyl maleamate and the N-dibutyl methyl maleamates.

The fumaramates, which can be used are those represented by the general formula f) as defined above. Typical fumaramates are methyl fumaramate, ethyl fumaramate, propyl fumaramate, n-butyl fumaramate, methyl N-methylfumaramate, ethyl N-methylfumaramate, the butyl N-methylfumaramates, methyl N-dimethylfumaramates, ethyl N-dimethylfumaramates, n-butyl N-dimethylfumaramate and the methyl N-dibutylfumaramates.

The citraconamates which can be used are those represented by the general formulas g) and h) as defined above. Typical citraconamates include, for example, methyl citraconamate, ethyl citraconamate, propyl citraconamate, the butyl citraconamates methyl N-methylcitraconamate, ethyl N-methylcitraconamates, propyl N-methylcitraconamates, n-butyl N-methylcitraconamate,

methyl N-dimethylcitraconamate, ethyl N-dimethylcitraconamate, n-butyl N-dimethylcitraconamate and the methyl N-dibutylcitraconamates.

The acrylates, which can be used are those represented by the general formula i) as defined above. Typical acrylates include, for example, methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate and butyl acrylate.

The vinyl esters which can be used are those represented by the general formula j) as defined above. Typical vinyl esters, include, for example, vinyl acetate, vinyl propionate, vinyl butyrate and vinyl isobutyrate.

Compounds represented by formula k) include those represented by formulas a) to j), formula k) being: —CH=C< , in addition to such other compounds as styrene, α -methylstyrene, *p*-acetaminostyrene, α -acetoxystyrene, vinyl chloride (when chloride monomer is vinylidene chloride), vinylidene chloride (when chloride monomer is vinyl chloride), vinyl sulphonamide ethyl vinyl ether, isopropyl vinyl ether, isopropenylmethyl ketone, ethyl isopropenyl ketone, methyl vinyl ketone, ethyl vinyl ketone, dimethyl maleate, diethyl maleate, diisopropyl maleate, dimethyl fumarate, diethyl fumarate, diisopropyl fumarate, acrylic acid, 2-vinyl pyridine, 4- and 5-vinyl pyridine, 2-methyl-5-vinyl pyridine, vinyl pyridines with alkyl groups in the 2, 4 or 6 positions, acrylic acid, methacrylic acid, methacrylamide, fumaronitrile, acrylonitrile, methylacrylonitrile, acetoxyacrylonitrile, N-vinylphthalimide, and ethylene and isobutylene. Especially useful polymerisable compounds coming within the scope of formula k) comprise those containing a $\text{CH}_2=\text{C<}$ group.

The copolymers of unsubstituted vinyl pyridine such as 2-vinyl pyridine and 4-vinyl pyridine as well as the substituted vinyl pyridines having one or more lower alkyl groups in the 2, 4 or 6 positions on the ring or similar vinyl pyridines with an acrylamide such as N-isopropyl acrylamide are particularly useful, desirably as the preformed non isolated or isolated polymer. These latter polymers when grafted with chloride component are characterized by an unusual degree of light fastness when dyed with any of the common textile dyes.

In one method of practising the present invention, a monomer represented by formulas a) to j), inclusive, is first homopolymerized, preferably until polymerization is substantially (90 to 100 percent.) complete although lower conversions such as 60% to 70% or lower are suitably employed with the unpolymerized monomer forming a portion of the monomeric material which is then polymerized with the chloride monomer in the second stage and, without separating the resulting polymer, the chloride monomer (alone or together with one

or more polymerizable monomers) is added and graft polymerization of the resulting mixture of monomer and homopolymer is effected.

In another method of practising the present invention from 1 to 99 percent. by weight of a monomer (I) selected from those represented by formulas a) to j) inclusive is first interpolymerized with from 99 to 1 percent. by weight of a different, monoethylenically-unsaturated, polymerizable compound (II) containing a $-\text{CH}=\text{C}<$ group, the percent. by weight being based on the combined weights of monomer (I) and compound (II), and, without separating the resulting interpolymer, the chloride monomer or monomers (alone or together with another polymerizable monomer) are added and the polymerization completed.

In a further method of practising the present invention, polymerization is effected of a mixture of from 5% to 95% by weight of a preformed isolated polymer which can be either a homopolymer of a compound represented by formulas a) to j) inclusive or an interpolymer of any of such compounds with each other or with a different, polymerizable ethenoid compound as hereinafter described and from 95% to 5% of monomeric material consisting of either chloride monomer alone, or a mixture of the chloride monomers, or a mixture of either or both of the chloride monomers with one or more ethenoid monomers which can include any of the compounds represented by formulas a) to j) as well as any of the other copolymerizable, monoethylenically unsaturated, ethenoid monomers described hereinafter. The preformed isolated polymer is dispersed or dissolved in a liquid medium and the chloride monomer (alone or together with another polymerizable monomer) is added and the polymerization completed.

In a further modification of the process of the present invention the graft polymers produced can be left in their reaction medium after the polymerization in accordance with the process of the invention has been effected, which preferably is substantially (90% to 100%) complete, and sufficient additional chloride monomer (corresponding to that in the polymer and the reaction medium) can be added and a final product containing from 60% to 95% by weight of chloride component and useful in the preparation of fibres of high softening point and ready susceptibility to dyeing obtained by polymerizing such additional monomer in the presence of the first-formed graft polymer in the polymerization mixture.

The amount of other monoethylenically-unsaturated, polymerisable compound used with the chloride monomers varies from 0% to 70%, based on the combined weights of the chloride monomer and the other monomer, i.e. the chloride monomer represents the "remain-

ing" 30% to 100% of the monomeric material polymerized with the preformed polymer. A particularly useful combination is one consisting of from 40 to 99 per cent. of the chloride monomer and from 60 to 1 percent of the other monomer.

The polymerizations are preferably carried out in the presence of a dispersing medium, such as water, mixtures of water with acetone, ethanol or dioxane, for example. By dispersing medium is meant a medium producing a true solution or a colloidal dispersion such as an emulsion.

Instead of using an aqueous dispersing medium as is disclosed in a number of the Examples below, it is possible to use organic solvents such as acetonitrile, aromatic hydrocarbons, e.g. benzene or toluene, liquid alkanes, e.g. n-heptane, aliphatic ethers or acetone. As noted above, organic solvents which are water soluble such as acetone can be used along with water in the polymerization.

The polymerization can be accelerated by heat, by actinic light and by the use of a polymerization catalyst. Such catalysts are commonly used in the art of polymerization and the present invention is not to be limited to any particular catalyst material. Catalysts which have been found to be especially useful comprise the peroxide polymerization catalysts, such as the organic peroxides (e.g. benzoyl peroxide, acetyl peroxide, acetyl benzoyl peroxide, lauryl peroxide, oleoyl peroxide, triacetone peroxide, urea peroxide, t-butyl hydroperoxide and alkyl percarbonates), hydrogen peroxide, perborates (e.g. alkali metal perborates, such as those of sodium or potassium) and persulphates (e.g. alkali metal and ammonium persulphates). Other catalysts such as the ketazines or azines can be used.

The quantity of catalyst used can be varied, depending on the monomer or amount of diluent, for example. Usually, from 0.1% to 5% by weight, based on the weight of monomers being polymerized, is sufficient for the purposes of the invention.

In the embodiments of the process of the present invention where the polymerization of the monomers takes place in the presence of non-isolated homo- or copolymers sufficient catalyst can be used to polymerize completely all monomers necessary for production of the final product, or an amount of catalyst sufficient to polymerize only the monomer or monomers in the first polymerization and additional catalyst added to complete the polymerization of the monomer, or monomers, in the second polymerization. The catalyst added to complete the second polymerization can be the same as that used in the first polymerization or it can be a different polymerization catalyst. It has been found that it is especially advantageous to use an amount of catalyst sufficient to polymerize only the first

monomer or monomers, and then upon addition of the second monomer or monomers, to add a further amount of catalyst at that time. This procedure provides a readier means for regulating the molecular weight distribution of the polymer composition.

The temperature at which the process of the invention can be carried out is not critical. Generally, a temperature of from 15° to 75° is sufficient.

If desired, emulsifying agents can be added to the reaction mixture to distribute uniformly the reactants throughout the reaction medium. Typical emulsifying agents include the alkali metal salts of certain alkyl acid sulphates (e.g. sodium lauryl sulphate), alkali metal salts of aromatic sulphonic acids (e.g. sodium isobutylnaphthalenesulphonate), alkali metal or amine addition salts of sulphosuccinic acid esters, alkali metal salts of fatty acids containing from 12 to 20 carbon atoms, sulphonated fatty acid amines, alkali metal salts of alkane sulphonic acids and sulphonated ethers, e.g. aryloxy polyalkylene ether sulphonates.

The polymerization can be carried out in the presence of chain regulators, such as hexyl, octyl, lauryl, dodecyl or myristyl mercaptans, which impart improved solubility properties to the polymer compositions. If desired, reducing agents such as alkali metal bisulphites (e.g. potassium or sodium bisulphites) can be added to reduce the time required for the polymerization to be effected.

The polymerization can be carried out batchwise but is more desirably carried out in continuous fashion.

In the discontinuous or batch-type processes, it is difficult to improve the solubility characteristics of the chloride graft polymers except by lowering the conversion percentage which is undesirable in many cases from the commercial standpoint in that the product yield for the reactor capacity is thereby lowered. Consequently, it is desirable to operate at high conversions, e.g. 90% or more, and still obtain the improved solubility characteristics.

Another difficulty encountered in batch processes, aside from the inherent disadvantages with regard to equipment, manpower, etc., is that the polymerizations, and particularly the free radical catalysed polymerization, usually exhibit an induction period before polymer formation is evidenced. The induction period appears to vary, even under carefully controlled conditions, and affects the molecular weight distribution of the polymer and hence the solubility and physical properties of the polymer.

Another disadvantage of the batch processes is the rapid evolution of heat by the large quantities of reactants which makes it almost impossible, even with efficient cooling, to hold a constant temperature during the course of the polymerization. In large scale commercial

production, this imposes a limit on the speed with which the polymerization can be carried out. Furthermore, certain amide modifiers, which are among the most useful for graft polymer formation, exhibit an inverse solubility in water and decrease in solubility as the temperature increases. Thus, most graft polymerizations with amide type modifiers, and particularly the acrylamide modifiers, must be carried out below the temperature at which the amide polymers become insoluble. If, as in a batch reaction, the temperature control is inadequate, the precipitation temperature of the preformed polymer is sometimes exceeded and discrete particles of the preformed polymer form and persist in the product. Accordingly, a nonhomogeneous composition distribution results with particles of ungrafted polymer present, and the properties of the product resemble those of a mechanical mixture.

A further disadvantage of batch processes is that usually the monomers employed vary somewhat in reactivity and rate of polymerization. Consequently, the relative proportions of the reactants is constantly changing during the polymerization and the composition distribution of the product is also changing. The first polymer formed tends to be relatively rich in the more reactive component and later polymer is progressively richer in the less reactive component. This, of course, results in non-uniform properties and is particularly serious when one of the components is introduced in a relatively small amount. Furthermore, the concentration of other ingredients also varies during the polymerization and hence the molecular weight of polymer being formed varies throughout the course of the reaction.

The products formed by continuous processes have a number of advantages. They are more homogeneous and have certain improved properties such as improved solubility over products obtained from analogous batch processes.

The various reactants and adjuvants are all continuously added to the polymerization system at controlled rates and in predetermined proportions depending upon the polymer composition desired. Polymerization in each increment of additive begins at once. When the continuous process is initiated, all of the components are added simultaneously and continuously at a specific rate which is thereafter maintained. During the initial stages of the process, product is not withdrawn until the volume of polymerization mixture has been built up to the desired capacity.

The continuous processes contemplated herein fall into two main groups: (1) those which are carried out in equipment which permits the continuous addition of reactants and the continuous removal of product (continuous process) and (2) those which are used in batch reactions wherein one or more of

the reactants is added continuously during the course of the polymerization, but from which no material is removed during the reaction (continuous batch process). In the preferred process, the chloride monomer alone or with another monomer or monomers containing a regulator such as tertiary dodecyl mercaptan is placed in a suitable storage or supply tank under an atmosphere of nitrogen. In another supply tank, under nitrogen, is charged air-free deionized water containing other reactants including the preformed polymer, which may have been isolated from or may be still present in its polymerization medium, the polymerization catalyst, and an acidic reagent such as phosphoric acid for regulating the pH of the reaction mixture. In a preferred process an emulsifier is included with the preformed polymer. A third tank contains the reducing agent or activator such as potassium metabisulphite in solution in air-free deionized water.

When non-isolated homo- or copolymers are used in the process of the invention these can also be formed continuously and the reaction mixture containing the unseparated polymer added continuously to the second step reactor.

If desired, of course, the monomers can be combined and in some cases it may even be desirable to premix the monomers and preformed polymer in the desired ratio and continuously feed the resulting admixture to the reaction zone. The polymerization can be carried out in several successive stages but best results from the standpoint of uniformity and solubility of product are obtained using but a single reaction stage.

The preferred procedure is to continuously draw the appropriate amounts of solutions or dispersions (such as emulsions) from the supply vessels into a reactor, subject the mixture to polymerizing conditions and continuously withdraw the graft polymer product from the reactor. By this means, the monomer or monomers are continuously graft polymerized with the preformed polymer at conversions of from 60% to 90% or more of the monomeric materials.

The length of time between the addition of any increment of reactants to the reactor and the removal of the polymer formed therefrom is defined as the contact time.

The contact time can be varied as desired depending upon the degree of conversion and the molecular weight of product desired. Product is then progressively withdrawn from the polymerization system in the form of an emulsion at a rate corresponding to the rate of addition of the reaction components. Consequently, each increment of the reaction mixture is present under identical reaction conditions for exactly the same time as any other increment. Furthermore, since all of the components of the reaction mixture are being continuously added, the relative concentrations in the system do not change and the entire

polymerization proceeds at equilibrium or in a steady state, and the product does not vary to any appreciable extent regardless of the length of time the process is carried on. One of the outstanding and unique features of this continuous equilibrium process is that differences in monomer polymerization rates have no effect whatever on the choice of polymer compositions or the uniformity of such polymer compositions. The monomer polymerization rates effect only the relationship of polymer composition to monomer feed rates at equilibrium; and, since the monomer feed rates can be adjusted to any desired value, polymer of any desired composition can be formed regardless of the relative polymerization rates of the monomers.

At equilibrium, the polymer emulsion or slurry is removed from the reactor by suitable means at the same total rate that the ingredients are being added from the supply tanks. Thus, the contact time in the reactor can be conveniently controlled by the absolute rate of addition of the reactants. Usually, the contact time is between 1 and 3 hours, although longer periods are advantageous in some cases. Although certain procedures are preferred as described above, the process can be varied in a number of ways. For example, the ingredients to be added can be combined or separated by using a smaller or larger number of supply tanks, with the practical minimum being two supply tanks, one for the activator and the other for the remaining ingredients.

In the commercial practice, of course, it is desirable to carry out the process for prolonged periods of time with continuous withdrawal of product and best results are obtained by carrying the reaction forward beyond the initial contact time. In some cases, however, when employing large volume equipment or preparing relatively small batches of polymer, it may be desirable to stop the polymerization when the reactor capacity is reached, and this can be done with somewhat less advantageous results, particularly when the contact time is such that the conversion is substantially complete.

Quite unexpectedly, the chloride graft polymers prepared by the continuous process of the present invention have greatly improved solubility characteristics even at high conversions where the batch process polymers are poorly soluble if soluble at all in many of the common organic solvents. Furthermore, even at low conversions of the order of 50-70% where batch process polymers have somewhat improved solubility, the graft polymers produced in accordance with this invention are superior in physical properties. This solubility of the modified vinyl chloride and vinylidene chloride graft polymers in such materials as acetone is particularly surprising because such polymers are well known to be difficultly soluble. Thus, even the vinyl chloride homo-

polymers and copolymers which are ordinarily much more soluble than the vinylidene chloride polymers, have been the subject of intensive work in the art to obtain acetone solubility.

5 In the case of the vinyl chloride polymers various devices were used to achieve acetone solubility, but they were all difficult or uneconomical to use in commercial production. Thus, for example according to British patent specification 651,155, ready solubility of 90%
10 vinylidene chloride-10% acrylonitrile copolymers is achieved only by employing specific ratios of ammonium persulphate catalyst to sodium metabisulphite activator and stopping the polymerization at 55-70% conversion. Similarly U.S. Patent 2,610,173 disclosed that
15 improved solubility in polymers of 80 to 98 percent acrylonitrile and 20 to 2 percent vinylidene chloride can be obtained only by carrying out the copolymerization at constant
20 reflux temperature with continuous addition of monomers in fixed relative proportions at rates which are varied to keep the mixture refluxing at constant temperature. Others
25 achieved solubility by continuous addition of monomer at constantly varying rates requiring close control of the conditions and continuous following of the polymer composition.

In contrast to these processes for preparing
30 simple vinyl chloride or vinylidene chloride homopolymers or copolymers (but not graft polymerization), the process of this invention merely involves adding all of the components including preformed polymer, monomer or
35 monomers, catalyst and such other polymerization aids as are desired at predetermined constant rates with the rate of product withdrawal also being constant and correlated to the rate of addition. In the stationary state
40 system embodying this invention, the relative ratios of preformed polymer, monomer or monomers, water and catalyst are uniform indefinitely, but the ratios chosen can be varied
45 infinitely and the monomers do not have to be added or removed differentially. Thus the system is always at equilibrium, although the point of equilibrium can be chosen as desired, since, for example, the contact time can vary
50 from 30 minutes to 24 hours or longer but is desirably of the order of about six hours or such time as the conversion is of the order of 90% or more. By a suitable choice of the ratio of monomers and polymers, any given
55 polymer composition can be obtained since the composition of the product will not deviate from the ratio of the reactants by more than 5%.

The preferred continuous process gives a highly uniform product having excellent
60 solubility characteristics. Thus, for example, graft polymers can be prepared with 15 to 25% by weight of preformed polymer, such as an acrylamide homo- or copolymer, and 85 to 75% by weight of monomeric material
65 consisting of 40 to 60% vinyl or vinylidene

chloride and 60 to 40% acrylonitrile and such polymers are readily soluble in acetone to give solutions from which textile fibres of high softening temperature, good tensile strength and elongation, good dyeability and non-inflammability can be readily spun by the usual fibre spinning techniques.

The continuous processes of the present invention are particularly suitable for preparing graft polymers wherein 60-95% of the polymer consists of the chloride component and 40-5% of the polymer consists of the modifier component, with the chloride monomer (i.e. vinyl chloride and/or vinylidene chloride) forming 15-100% and preferably
70 75 80 30-100% of the chloride component.

The exact reason for the greatly improved solubility characteristics of the graft polymers prepared in accordance with this invention is not clearly apparent but such improved properties would appear to be a function of the unusual uniformity of the polymer from the standpoint both of composition distribution and molecular weight distribution. Although the preferred polymers are soluble in acetone at room temperature, the invention is not limited to acetone-soluble polymers since improved solubility in other well known solvents such as N,N-dimethyl formamide, N,N-dimethyl acetamide, γ -butyrolactone, alcohols, aromatic hydrocarbons and the like characterizes the products produced in accordance with the invention. Thus, for example, spinning
85 90 95 100 dopes may be used wherein the solvent is a mixture of such materials as acetone and an alkyl alcohol with excellent results.

Although the continuous process is preferred a batch or continuous batch process can be employed with good results. In the continuous
105 110 115 120 batch processes, the various ingredients of the polymerization mixture can be added to the reactor in various ways. Thus, the catalyst, activator, isolated polymer and water, can be charged to the reactor in a batch and the monomeric material and regulator added continuously; the monomeric material, regulator, catalyst, isolated polymer and water, can be charged to the reactor and the activator added continuously; the monomer, regulator, activator isolated polymer and water, can be charged to the reactor and the catalyst added continuously; or the monomer, isolated polymer, regulator and water, can be charged to the reactor and the catalyst and activator added continuously, either together or separately. 'Non-isolated' may replace 'isolated' polymer.

The polymer compositions of the present invention contain from 5 to 95 percent-by weight of chloride component (i.e. vinyl or vinylidene chloride alone or in admixture with each other or in admixture with one or more polymerizable monomers and from 95 to 5 percent by weight of the homo- or interpolymer component (homopolymer of compound
125 130

(I) or interpolymers of compound (II) with monomer (I), which is a compound selected from those of formulas a) to j) above), based on the combined weights of these components.

5 The following Examples illustrate but do not limit the process of the present invention.

EXAMPLE 1.

4 grams of N,N-dimethyl acrylamide were added to 100 mls. of water containing 0.01 gram of potassium persulphate and 0.01 gram of sodium bisulphite. Polymerisation was completed by heating at 35° C. for 12 hours. 1 gram of acrylonitrile and 5 grams of vinylidene chloride, 0.1 gram potassium persulphate, 0.1 gram sodium bisulphite and 1 ml. of Tergitol No. 4 (an aryloxy polyalkylene sulphonated ether) were added to the cooled reaction mixture and the polymerisation was completed by heating at 35° C. for an additional 8 hours. The resultant polymer was soluble in such solvents at γ -butyrolactone and dimethylacetamide.

Fibres obtained from this polymer had a softening point about 190° C. and showed excellent affinity for dyes.

EXAMPLE 2.

4 grams of N,N-dimethyl acrylamide were added to 100 ml. of water containing 0.01 gram of potassium persulphate and 0.01 gram of sodium bisulphite. Polymerisation was completed by heating at 35° C. for 12 hours. 1.8 gram of acrylonitrile and 4.2 grams of vinyl chloride, 0.1 gram potassium persulphate and 0.1 gram of sodium bisulphite were added to the cooled reaction mixture and the polymerization was completed by heating at 35° C. for an additional 8 hours. The resultant polymer was soluble in such solvents as cyclohexanone, methylethylketone and dimethylformamide. Fibres obtained from this polymer showed excellent affinity for dyes.

EXAMPLE 3.

2 grams of N-isopropyl acrylamide were added to 100 mls. of water containing 0.5 gram potassium persulphate and 0.5 gram sodium bisulphite and 1 gram of orthophosphoric acid. Polymerization was completed by heating at 35° C. for 12 hours. 6.4 grams of vinylidene chloride and 1.6 gram vinyl acetate, 0.1 gram potassium persulphate, 0.1 gram sodium bisulphite and 1 ml. of Tergitol No. 4 were added to the cooled reaction mixture and the polymerization completed by heating at 35° C. for an additional 8 hours. The precipitated polymer was obtained in a 90 percent yield and contained 18 percent amide by analysis. The polymer was soluble in such solvents as dimethylacetamide and dimethylformamide.

60 The fibres obtained from this polymer had a softening point above 200° C. and showed excellent affinity for dyes.

EXAMPLE 4.

9.5 grams of N,N'-dimethyl fumaramide were suspended in 100 ccs. of distilled water

along with 0.1 gram of ammonium persulphate 0.1 gram of sodium bisulphite and 1 gram of Triton 720 (7-ethyl-2-methyl-undecane-4-sulphonic acid). The resulting emulsion was allowed to polymerize for 16 hours at 50° C., and then cooled down to room temperature. 0.5 gram of vinyl chloride, 0.01 gram of ammonium persulphate and 0.01 gram of sodium bisulphite were then added and the polymerization completed by tumbling at 50° C. for 8 hours. The emulsion was broken by the addition of a concentrated salt solution and the precipitated polymer was filtered, washed and dried.

Fibres were prepared from a mechanical mixture containing 30 percent by weight of the polymer obtained and 70 percent by weight of polyvinyl chloride by extruding a solution of the mixture in dimethyl formamide into a precipitating bath.

EXAMPLE 5.

2 grams of N,N'-dimethyl maleamide were suspended in 18 ccs. of water along with 0.02 gram of ammonium persulphate, 0.02 gram of sodium bisulphite and 1 gram of Triton 720. The resulting emulsion was allowed to polymerize for 8 hours at 25° C., then cooled down to room temperature and 7 g. of vinyl chloride, 1 g. of vinyl acetate, 0.1 g. of ammonium persulphate, 0.1 g. of sodium bisulphite and 2 g. of Triton 720 in 50 cc. of water were added. After tumbling the reaction mixture at 45° C. for 6 hours, the polymer product was precipitated by the addition of an aqueous solution of sodium chloride to give 9.7 g. of polymer product containing 20 percent by weight of N,N'-dimethyl maleamide.

Fibres spun from the above polymer from a solution in dimethyl formamide had a softening temperature above 165° C. and showed excellent affinity for dyes.

EXAMPLE 6.

2 g. of N-methyl methyl fumaramate were emulsified in 50 cc. of water containing 1 g. of Triton 720 and 0.05 g. of ammonium persulphate. The resulting emulsion was heated at 50° C. for 12 hours, cooled to room temperature and a monomer composition containing 4 grams of vinylidene chloride, 4 grams of acrylonitrile, 0.1 gram of ammonium persulphate and 0.1 gram of sodium bisulphite was added. The reaction mixture was allowed to stand at 25° C. for 12 hours. The precipitated polymer weighed 9.4 grams and contained 19.3 percent by weight of N-methyl fumaramate.

Fibres obtained from this polymer had a softening point above 150° C. and showed excellent affinity for dyes.

EXAMPLE 7.

1 gram of N-isopropyl methyl maleamate was emulsified in 10 cc. of water containing 0.5 gram of potassium laurate, 0.01 gram of potassium persulphate and 0.01 gram of

sodium bisulphite. The resulting emulsion was heated 12 hours at 35° C. and 16 grams of vinyl chloride, 3 grams of isopropenyl acetate, 0.1 gram of potassium persulphate, 0.1 gram of sodium sulphite and 2 grams of potassium laurate in 100 cc. of water were added and the polymerisation was continued for an additional 8 hours at 35° C. The precipitated polymer product was obtained in a 92 percent yield and contained approximately 5 percent by weight of N-isopropyl methyl maleamate. The polymer was soluble in N,N-dimethyl formamide or N,N-dimethyl acetamide.

15 Fibres obtained from these solutions had a sticking temperature above 160° C. and showed excellent dye affinity.

EXAMPLE 8.

3 grams of methyl citraconamate, 0.1 gram of ammonium persulphate and 0.1 gram of sodium bisulphite and 1 gram of Triton 720 were added to 50 cc. of distilled water. The resulting emulsion was then heated for 12 hours at 45° C. with tumbling. An emulsion of 15 grams of vinylidene chloride, 2 grams of methacrylonitrile, 0.2 gram of ammonium persulphate and 0.2 gram of sodium bisulphite in 50 cc. of distilled water containing 2 grams of Triton 720 was then added. The reaction mixture was then heated for an additional 8 hours at 35° C. The resulting polymer was obtained in a 93 percent yield and contained 14.9 percent by weight of methyl citraconamate on analysis.

35 Fibres obtained by extruding a solution of the polymer obtained above in N,N-dimethyl formamide had a sticking temperature above 175° C. and showed excellent affinity for dyes.

EXAMPLE 9.

2 grams of vinyl acetate was suspended in 18 cc. of water along with 0.02 gram of ammonium persulphate, 0.02 gram of sodium bisulphite and 1 gram of Triton 720. The resulting emulsion was allowed to polymerize for 16 hours at 50° C., then cooled down to room temperature. 8 grams of vinylidene chloride, 0.1 gram of ammonium persulphate and 0.1 gram of sodium bisulphite and 2 grams of Triton 720 in 50 cc. of water were added. After tumbling the reaction mixture at 50° C. for 2 hours, the polymer product was precipitated by the addition of an aqueous solution of sodium chloride to give 9.6 grams of polymer product containing 19.9 percent by weight of vinyl acetate based on analysis.

This polymer can be mixed with polyvinylidene chloride in all proportions and dissolved to give stable solutions which do not separate into distinct layers on standing and from which fibres and films of homogeneous character can be spun, extruded or cast.

EXAMPLE 10.

2 grams of citraconamide, 0.05 gram of potassium persulphate and 1 cc. of Tergitol

No. 4 were added to 30 cc. of water. The resulting emulsion was then tumbled at 50° C. for 12 hours, at the end of which time 8 grams of vinyl chloride, 0.1 gram of potassium persulphate, 2 cc. of Tergitol No. 4 and 70 ccs. of water were added. The reaction mixture was then tumbled for an additional 12 hours at 45° C. The resulting polymer was obtained in a 93 percent yield and contained 18 percent by weight of citraconamide on analysis. It was soluble in either N,N-dimethyl formamide or N,N-dimethyl acetamide.

EXAMPLE 11.

2.5 grams of N,N-dimethyl acrylamide was added to 100 mls. of water containing 0.01 gram of potassium persulphate and 0.01 gram of sodium bisulphite. Polymerisation was completed by heating at 35° C. for 12 hours. 3.0 grams of vinyl chloride and 4.5 grams of methacrylonitrile, 0.1 gram of sodium bisulphite, and 0.1 gram of potassium persulphate and 1 ml. of Tergitol No. 4, were added to the cooled reaction mixture, and the polymerisation was completed by heating at 35° C. for an additional 8 hours. The resultant precipitated, isolated, and dried polymer was soluble in solvents such as dimethylformamide. Fibres obtained therefrom had a softening point above 190° C., showed excellent affinity for dyes, and were noninflammable.

EXAMPLE 12.

The advantageous properties of the fibre-forming chloride polymers as well as the non-flammable characteristics are retained with the chloride component containing 30—100% by weight of vinyl or vinylidene chloride and 70—0% of another ethenoid monomer. Thus, 2.5 grams of isopropyl acrylamide was added to 100 mls. of water containing 0.5 gram potassium persulphate, 0.5 gram of sodium bisulphite, and 1 gram of orthophosphoric acid. Polymerisation was completed by heating at 35° C. for 12 hours. 2.25 grams of vinylidene chloride and 5.25 grams of acrylonitrile, 0.1 gram of potassium persulphate, 0.1 gram of sodium bisulphite, and 1 ml. of Tergitol No. 4 were added to the cooled reaction mixture, and the polymerisation was completed by heating at 35° C. for an additional 8 hours. The precipitated polymer was obtained in 90% yield.

Fibres obtained from this polymer had a softening point of 200° C., showed an excellent affinity for dyes, and were non-inflammable.

EXAMPLE 13.

2 grams of vinyl acetate and 0.2 gram of acrylonitrile were emulsified in 80 ccs. of water containing 0.01 gram of ammonium persulphate and 0.01 gram of sodium bisulphite and 3 grams of Triton 720. The resulting emulsion was heated at 35° C. for 6 hours. After cooling to room temperature, 7.8 grams of vinyl chloride, 0.1 gram of ammonium persulphate and 0.1 gram of sodium bisulphite

were added. The reaction mixture was then tumbled end over end for 12 hours at 50° C. The product was filtered off, washed with water and dried. It contained 77.9 percent by weight of vinyl chloride based on analysis.

EXAMPLE 14.

1 gram of acrylamide and 2 grams of N-methyl acrylamide were added to 100 mls. of water containing 0.05 grams of potassium persulphate and 1 gram of orthophosphoric acid. Polymerization was completed by heating at 50° C. for 12 hours. 4.2 grams of vinyl chloride, 2.8 grams of acrylamide, 0.1 gram of potassium persulphate and 0.1 gram of sodium bisulphite were added to the cooled reaction mixture and the polymerisation completed by heating at 35° C. for an additional 8 hours. Precipitated polymer was obtained with a 95 percent yield and was soluble in such solvents as acetone, methylethylketone and cyclohexanone.

Fibres obtained from this polymer showed excellent affinity for acetate, wool, direct and vat dyes.

EXAMPLE 15.

1 gram of acrylamide and 2 grams of N-methyl acrylamide were added to 100 mls. of water containing 0.5 grams potassium persulphate and 1 gram orthophosphoric acid. Polymerization was completed by heating at 50° C. for 12 hours. 5 grams of vinylidene chloride and 2 grams of acrylamide, 0.1 grams potassium persulphate, 0.1 grams sodium bisulphite and 1 ml. of Tergitol No. 4 were added to the cooled reaction mixture and the polymerization completed by heating at 35° C. for an additional 8 hours. The precipitated polymer was obtained in 95 percent yield and was soluble in such solvents as dimethylacetamide and dimethylformamide.

Fibres obtained from this polymer showed excellent affinity for dyes and had a softening point above 185° C.

EXAMPLE 16.

2.5 grams of fumaramide and 0.5 gram of acrylonitrile were emulsified in 75 ccs. of distilled water containing 0.05 gram of ammonium persulphate, 0.05 gram of sodium bisulphite and 1 gram of Triton 720. The resulting emulsion was then heated at 35° C. for 12 hours. There was then added 6 grams of vinyl chloride, 1 gram of vinyl acetate, 0.1 gram of ammonium persulphate and 0.1 gram of sodium bisulphite, and the polymerization mixture was heated at 35° C. for an additional 12 hours. The precipitated polymer was obtained in a 93 percent yield and contained 59.5 percent by weight of vinyl chloride based on analysis.

Fibres spun by extruding a solution of the polymer product in cyclohexanone into a precipitating bath had a softening point above 145° C., an extensibility of 33 percent and showed excellent affinity for dyes.

EXAMPLE 17.

1.3 grams of N,N-dimethyl ethyl fumarate and 1 gram of methyl fumaramate were suspended in 20 ccs. of distilled water containing 0.02 gram of ammonium persulphate and 0.02 gram of sodium bisulphite and 1 gram of Triton 720. The resulting emulsion was then heated at 50° C. for 16 hours. After cooling to room temperature, a dispersion of 7 grams of vinyl chloride, 0.7 gram of dimethyl fumarate, 0.1 gram of ammonium persulphate, 0.1 gram of sodium bisulphite and 1 gram of Triton 720 in 50 ccs. of water was added. The dispersion was tumbled end over end at 50° C. for an additional 12 hours. The precipitated polymer weighed 9.4 grams and contained approximately 70 percent by weight of vinyl chloride based on analysis.

Fibres spun by extruding a solution of the polymer product in γ -butyrolactone into a precipitating bath had a softening point above 155° C. and showed good dye affinity.

EXAMPLE 18.

1 gram of acrylonitrile and 2 grams of N-methyl acrylamide were added to 100 ccs. of distilled water having dissolved therein 0.05 gram of potassium persulphate and 1 gram of ortho phosphoric acid. The solution was then heated at 50° C. for 12 hours. There was then added 7 grams of vinyl chloride, 0.1 gram sodium bisulphite and 0.1 gram of potassium persulphate to the cooled reaction mixture and heating was resumed for 8 hours at 35° C. The precipitated polymer was obtained in a 92 percent yield and contained 69.5 percent vinyl chloride based on analysis.

Fibres spun by extruding a solution of the polymer product in N,N-dimethyl formamide into a precipitating bath had a softening point above 175° C. and showed excellent dye susceptibility.

EXAMPLE 19.

1 gram of acrylamide and 2 grams of N-methyl acrylamide were added to 100 mls. of water containing 0.05 gram of potassium persulphate plus 1 gram of orthophosphoric acid. Polymerization was completed by heating at 50° C. for 12 hours. 3.0 grams of vinyl chloride, 4.5 grams of methacrylonitrile, 0.1 gram of potassium persulphate, and 0.1 gram of sodium bisulphite were added to the cool reaction mixture and the polymerization was completed by heating at 35° C. for an additional 8 hours. The precipitated polymer was isolated by filtration, and was washed and dried. Fibres obtained from this polymer showed an excellent affinity for acid wool and direct dyes and were noninflammable.

EXAMPLE 20.

2 grams of poly N-methyl acrylamide were dissolved in 100 ccs. of water containing 0.1 gram of ammonium persulphate, 0.1 gram of potassium bisulphite and 8 grams of vinyl chloride. The resulting dispersion substantially of vinyl chloride in a solution of the polymer

was allowed to polymerize for 16 hours at 25° C. The resulting polymer was filtered off. After drying, there was obtained a product weighing 9.3 grams and was found to contain 19 percent by weight of N-methyl acrylamide on analysis.

Solutions of our new compositions of matter are readily spun into fibres by dry spinning or by wet spinning into suitable coagulating baths. Fibres obtained by preparing a solution of the polymer obtained above in dimethylformamide and extruding the solution into a precipitating bath had a tenacity of 3.5 grams per denier, an extensibility of 32 percent and a sticking temperature above 165° C.

EXAMPLE 21.

1 gram of poly N-isopropyl acrylamide was added to 60 ccs. of water containing 1 cc. of Tergitol No. 4. The mixture was then tumbled end over end for 1 hour at 50° C. The solution was cooled and 8 grams of vinyl chloride, 0.5 gram of methyl acrylate, 0.1 gram of ammonium persulphate and 0.1 gram of sodium bisulphite were added. The polymerization was effected by tumbling for 12 hours at 25° C. The polymer was obtained in a 93 percent yield and contained approximately 9 percent isopropyl acrylamide on analysis.

Fibres spun by extruding a solution of this polymer in dimethylacetamide into a precipitating bath had a tenacity of 3.6 grams per denier, an extensibility of 28 percent and a sticking temperature above 160° C.

EXAMPLE 22.

3 grams of an interpolymers of N,N-dimethyl acrylamide and vinyl acetate containing 60 percent by weight of N,N-dimethyl acrylamide were dissolved in 50 ccs. of a 50 percent solution of acetonitrile in water. There were then added 3 grams of vinylidene chloride, 3 grams of vinyl acetate, 0.1 gram of ammonium persulphate and 0.1 gram of sodium bisulphite. The polymerization was effected by heating for 12 hours at 40° C. The precipitated polypolymer was obtained in a 92 percent yield and contained approximately 29 percent by weight of the amide-vinyl acetate interpolymers upon analysis.

Fibres spun by extruding a solution of the polymer in acetone into a precipitating bath had a tenacity of 3.1 grams per denier, an extensibility of 43 percent and a sticking temperature above 120° C. The fibres showed an excellent affinity for acetate, direct, vat and acid dyes. This polymer can be mixed with polyvinylidene chloride or copolymers of vinylidene chloride containing 50 percent or more of vinylidene chloride in all proportions and dissolved to give stable solutions which do not separate into distinct layers on standing and from which fibres and films of homogeneous character can be spun, extruded or cast.

EXAMPLE 23.

2 grams of an interpolymers of N-methyl

acrylamide and acrylamide containing 30 percent by weight of N-methyl acrylamide were added to 70 ccs. of water containing 0.1 gram of sodium bisulphite, 0.1 gram of ammonium persulphate, 5.4 grams of vinyl chloride and 3.6 grams of acrylonitrile. The resulting dispersion substantially of vinyl chloride in a solution of the polymer and acrylonitrile was then polymerized for 16 hours at 35° C. The polymer was filtered off and then dried. It was obtained in a 93 percent yield and was found to contain 17 percent by weight of N-methyl acrylamide interpolymers on analysis.

Fibres spun by extruding a solution of this polymer in dimethylformamide into a precipitating bath had a softening point above 145° C. and showed excellent dye affinity.

EXAMPLE 24.

3 grams of an interpolymers of acrylamide and methyl acrylate containing 80 percent by weight of acrylamide was dissolved in 100 ccs. of water containing 0.1 gram of potassium persulphate, 0.1 gram of sodium bisulphite, 6 grams of vinylidene chloride and 1 gram of acrylonitrile. The resulting dispersion substantially of vinylidene chloride in a solution of the polymer and acrylonitrile was then heated for 16 hours at 35° C. The solution was cooled to room temperature and the precipitated polymer filtered off, washed with distilled water and finally dried. It was obtained in a 93 percent yield and was found to contain approximately 29.5 percent by weight of the acrylamide-methyl acrylate interpolymers on analysis.

Fibres obtained from this polymer had a sticking temperature above 185° C. and showed excellent affinity for dyes.

EXAMPLE 25.

1 gram of poly-methyl fumaramate was added to 60 ccs. of water containing 1 cc. of Tergitol No. 4. The mixture was then tumbled end over end for 1 hour at 50° C. The solution was cooled and 7 grams of vinyl chloride, 2 grams of N-methyl acrylamide, 0.1 gram of ammonium persulphate and 0.1 gram of sodium bisulphite were added. The polymerization was effected by tumbling for 16 hours at 25° C. The polymer was obtained in a 93 percent yield and contained 10 percent by weight of methyl fumaramate.

Fibres spun from the above polymer had a softening point above 160° C. and showed excellent affinity for dyes.

EXAMPLE 26.

3 grams of an interpolymers of N-methyl methyl maleamate and vinyl acetate containing 60 percent by weight of N-methyl methyl maleamate was dissolved in 50 ccs. of a 50 percent solution of acetonitrile in water. There were then added 6 grams of vinyl chloride, 0.1 gram of ammonium persulphate and 0.1 gram of sodium bisulphite. The polymerization was effected by heating for 16 hours at 40° C. The precipitated polymer was obtained

in a 92 percent yield and contained 29 percent by weight of the amide-vinyl acetate interpolymer upon analysis.

5 Fibres obtained from the polymer had a softening temperature above 165° C. and showed excellent affinity for dyes. Fibres obtained from a solution of a mechanical mixture of 25 parts polyvinyl chloride and 75 parts of the above-described polymer and extruding the solution into a precipitating bath
10 had a tenacity of 3.8 grams per denier, an extensibility of 29 percent and a sticking temperature above 165° C.

EXAMPLE 27.

15 4 grams of poly N,N-dimethyl ethyl citraconamate was dissolved in 75 ccs. of acetonitrile containing 3.5 grams of vinylidene chloride, 3 grams of vinyl chloride and 0.3 gram of benzoyl peroxide. The resulting solution was then heated for 24 hours at 50° C. and then cooled. The precipitated polymer was collected on a filter, washed and dried. It was found to contain approximately 39 percent by weight of N,N-dimethyl ethyl citraconamate on analysis.

25 Fibres obtained from this polymer had a sticking temperature above 155° C. and showed excellent dye affinity.

EXAMPLE 28.

30 2 grams of poly N,N'-di-isopropyl maleamide was emulsified in 80 ccs. of water containing 3 ccs. of Tergitol No. 4. There was then added 6.5 grams of vinyl chloride, 1.5 grams of dimethyl maleate, 0.1 gram of potassium persulphate and 0.1 gram of sodium bisulphite. The emulsion was then heated at 35° C. for 16 hours with tumbling. The emulsion was then cooled to room temperature, the precipitated polymer filtered off, washed
40 with distilled water and dried. It was found to contain 20.5 percent by weight of the maleamide.

45 Fibres spun by extruding a solution of this polymer in dimethyl acetamide into a precipitating bath had a tenacity of 3.9 grams per denier, an extensibility of 29 percent and shrank only 10 percent in boiling water.

EXAMPLE 29.

50 The improved properties of the chloride polymers embodying the invention are obtained even when the chloride monomer amounts to less than 50% of the monomeric material. Thus, the chloride monomer can form as low as 30% of the monomeric material in fibre forming polymers and give fibres which are non-inflammable. For example, 2.5 grams of poly-N-isopropylacrylamide was dissolved in 100 ccs. of water containing 0.1 gram of potassium persulphate, 0.1 gram of potassium metabisulphite, 2.25 grams of vinylidene chloride and 5.25 grams of acrylonitrile. The resulting dispersion substantially of vinylidene chloride in a solution of the polymer and acrylonitrile was then heated for 16 hours at
65 35° C., at the end of which time it was heated

to 75° C. The precipitated polymer was isolated by filtration, and was washed and finally dried.

70 Fibres obtained therefrom had a bar sticking temperature of 195° C., showed an excellent affinity for dyes, and were non-inflammable.

75 The following Examples illustrate the continuous form of the process of the present invention.

EXAMPLE 30.

80 In a typical continuous equilibrium process embodying the present invention, vinylidene chloride monomer (A), acrylonitrile monomer (B), a 1% aqueous solution (C) of potassium persulphate, and a dispersion (D) of 100 parts by weight of water containing 2 parts by weight of an isolated N-isopropyl acrylamide-2-methyl-5-vinyl pyridine copolymer together with 1 part by weight of dioctyl sodium sulphosuccinate (Aerosol OT) and 0.1 part by weight of potassium metabisulphite were stored separately and added continuously to a reactor at such rates that the relative ratios by weight of materials entering the reactor were 1.0 (A): 1.0 (B): 0.5 (C): 24.0 (D). The materials admixed in the reactor were agitated vigorously and the temperature was held constant at 25° C. Polymerization ensued almost immediately on admixture of the first increment of reactants and continued with the continuous addition. The contact time, that is the time between introduction of any increment to the reactor and its withdrawal as product, is in practice the volume of the reactor divided by the rate of introduction of the ingredients. Since, at equilibrium, the polymer emulsion or slurry is removed from the reactor at the same total rate as the ingredients are being added, the contact time is conveniently controlled by the absolute rate of addition of the reactants. Thus, the contact time can be varied infinitely depending upon the rate of addition chosen. An especially useful contact period was about 6 hours, at which time titration for residual acrylonitrile monomer indicated that a conversion to polymer of 90% had occurred. Thus, the rate of addition in the preferred process was chosen so that with continuous addition of the ingredients in the ratio set out, the reactor filled in 6 hours at which time continuous withdrawal of polymer emulsion was begun at the same rate as the total rate of addition of the reaction ingredients. The polymeric product removed was then isolated, a particularly convenient method being to heat the emulsion above its precipitation temperature or to about 60-70° C. and filtering out the resultant precipitated product. Thus, throughout the process, the polymerization proceeded in an equilibrium or stationary state wherein the ratio of all of the ingredients remained unchanged. The process could be continued indefinitely without any change in polymer uni-
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formity and with no control being necessary beyond maintaining the rates of addition and withdrawal constant. The graft polymer product, which could be isolated by any of the usual methods, was soluble in acetone and stayed in solution at room temperature at spinning dope concentrations of 15—20% solids, which was in marked contrast to graft polymers of the same composition but prepared by batch processes which were not soluble in acetone. Spinning dopes of the polymer were dry spun into fibres having a tenacity of 3 grams per denier, a softening point of 190° C. and a high affinity for most classes of dyes.

EXAMPLE 31.

Vinyl chloride (A), acrylonitrile (B), a 1% aqueous solution (C) of potassium persulphate, and a dispersion (D) of 2 parts of N-isopropyl acrylamide-2-methyl-5-vinyl pyridine copolymer, 1 part of sodium octyl sulphate, and 0.1 part of potassium metabisulphite in 100 parts of water were continuously added to a stirred reactor in a weight ratio of 0.6 (A): 1.4 (B): 0.5 (C): 12.0 (D). The temperature of the resulting mixture was maintained at 25° C. and the rate of addition of the materials A—D was set to give a contact time of about 24 hours, at which time a titration for residual acrylonitrile indicated a conversion to polymer of about 90% was occurring. Thereupon, the polymer emulsion was withdrawn at the same rate of addition of the various ingredients. The resultant graft polymer product, after isolation by the usual methods, was dry spun into fibre. The resulting fibres after drafting, relaxing and stabilization in accordance with usual practice had a tenacity of 2.8 grams per denier, an extensibility of 30% and a high affinity for most classes of dyes such as cellulose acetate dyes. The fibres were non-inflammable and were of excellent utility for the manufacture of textiles of any desired colour or shade.

Similarly improved results are obtained with other polymers prepared in accordance with the process of the present invention. The polymers obtained can be compounded with the usual compounding materials if desired such as pigments, dyes, fillers, softeners and the like in accordance with usual practices.

The continuous process of the present invention provides graft polymers of improved solubility characteristics whereby more common solvents such as acetone or the like can be used in preparing dopes. Such solvents as acetone are more economical to use and pose fewer recovery and handling problems. Furthermore, when acetone soluble polymers are obtained, it is possible to utilize equipment which is suitable for use for spinning cellulose acetate fibres and similar acetone-soluble fibres. This increased versatility is of great commercial significance. Furthermore, it is desirable to be able to control the solubility charac-

teristics as desired according to a predetermined plan.

Other solvents which can be used for the preparation of fibres from the new polymers of the present invention include ethylene carbonate, ethylene carbamate, γ -butyrolactone, N-methyl-2-pyrrolidone, N,N-dimethyl methoxyacetamide, dimethylcyanamide, N,N-dimethylcyanoacetamide, N,N-dimethyl- β -cyanopropionamide, glycolonitrile (formaldehyde cyanohydrin), malonoitrile, ethylenecyanohydrin, dimethylsulphoxide, dimethyl sulphone, tetramethylene sulphone, tetramethylene sulphoxide, N-formylpyrrolidine, N-formylmorpholine and N,N'-tetramethylmethanephosphonamide. We have found that N,N-dimethylformamide and N,N-dimethylacetamide are usually particularly advantageous. The amount of polymer dissolved in the solvent can vary from about 10 to 40 percent by weight.

The graft polymers of the invention are also more soluble in many organic solvents compared with polyacrylonitrile polymers. This enhanced solubility is readily achieved at low conversions using batch processes. At conversions of 90% or more, polymers having good solubility in solvent such as acetone are readily prepared by the continuous processes of the invention. The mechanical properties of the fibres of the invention are also excellent.

The fibres of the present invention usually have a higher softening point than the known copolymers mentioned above and do not exhibit the segmentation defect shown by many of the fibres prepared from certain prior art mixtures comprising polyvinyl chloride or polyvinylidene chloride. These fibres also have a higher softening point than fibres prepared from simple interpolymers of vinyl chloride or vinylidene chloride with monomers which have the property of imparting dye affinity to the polymer products.

Because of their excellent compatibility, the graft polymers of the invention can be used in mechanical mixtures with other polymeric materials to give improved solubility and dyeability characteristics.

The graft polymers of the invention containing from 60% to 95% by weight of the chloride component are useful as fibre forming materials and are compatible with polyvinyl chloride or polyvinylidene chloride (the monomer of the chloride component corresponding to that of the polyvinyl or polyvinylidene chloride), forming substantially homogeneous compositions. These polymers can contain from 30% to 95% by weight of the chloride component and still be non-inflammable. Thus fibres formed from these polymers can be woven into textile fabrics which will not sustain combustion in themselves, a characteristic of considerable utility in the textile field and particularly as regards wearing apparel. The polymers containing from 5 to 60% by weight

of chloride component can be added directly to polymers containing at least 85% by weight of vinyl chloride or vinylidene chloride units to form compatible mixtures useful for fibre applications.

The graft polymers of the invention can also be used in the manufacture of cast or extruded sheets, films, tapes and ribbons. In film form, the polymers can be employed in photographic applications such as for film base for carrying photosensitive emulsions, such as silver halide emulsions, and such use can be in the manufacture of either black-and-white or colour photographic film.

"Tergitol" and "Triton" are registered trade marks.

WHAT WE CLAIM IS:—

1. A process for preparing a graft polymer which comprises polymerising in a liquid medium from 95% to 5% by weight of a monomer composition (1) containing from 30% to 100% by weight of vinylidene chloride or vinyl chloride or a mixture of said chlorides and from 70% to 0% by weight of a different monoethylenically unsaturated, polymerisable compound containing a $-\text{CH}=\text{C}-$ group with from 5% to 95% by weight of a polymer formed by polymerising a monomer composition (2) containing from 1% to 100% by weight of a monomer represented by any of formulas (a) to (j) as herein defined and from 99% to 0% by weight of a different, monoethylenically unsaturated, polymerisable compound containing a $-\text{CH}=\text{C}-$ group and which has or has not been isolated from its polymerisation medium, the said percentages by weight of monomer compositions (1) and (2) being based on the total weight of these compositions (1) and (2).

2. A process according to claim 1 in which composition (1) contains acrylonitrile, methacrylonitrile, vinyl acetate, methyl acrylate, acrylamide or methacrylamide.

3. A process according to claim 1 or 2 in which composition (2) contains N,N-dimethyl acrylamide, N-methyl acrylamide, N-isopropyl acrylamide or acrylamide.

4. A process according to any of claims 1 to 3 in which composition (2) contains acrylonitrile.

5. A process according to claim 1 in which composition (1) contains acrylonitrile or methacrylonitrile and composition (2) contains an acrylamide.

6. A process according to claim 1 or 2 in which composition (2) contains N-isopropyl acrylamide and 2-methyl-5-vinyl-pyridine.

7. A process according to any of claims 1 to 6 in which composition (2) contains at least 50% by weight of the monomer or monomers represented by formulas a) to j).

8. A process according to any of the preceding claims in which composition (1) contains from 40% to 99% of said chloride monomer or monomers.

9. A process according to claim 1 in which composition (1) contains from 30% to 99% by weight of vinylidene chloride or vinyl chloride and from 70% to 1% of acrylonitrile or methacrylonitrile and composition (2) contains an acrylamide.

10. A process according to any of claims 1 to 5 in which composition (1) contains from 40% to 60% vinyl chloride or vinylidene chloride and from 60% to 40% acrylonitrile.

11. A process according to claim 1 in which composition (1) contains vinyl chloride and composition (2) contains from 1% to 99% by weight vinyl acetate and from 99% to 1% acrylonitrile.

12. A process according to any of the preceding claims in which from 95% to 60% of composition (1) and from 5% to 40% of composition (2) is employed.

13. A process according to claim 12 in which from 85% to 75% of composition (1) and from 15% to 25% of composition (2) is employed.

14. A process according to claim 1 in which the monomers of compositions (1) and (2) are those specified in any one of Examples 7, 13, 16, 17, 18, 21, 22 and 28.

15. A process according to any of the preceding claims wherein portions of composition (1) and portions of polymer formed by the polymerisation of composition (2) are brought together successively and continuously and in constant ratio by weight in the range from 5% to 95% by weight of said composition and from 95% to 5% by weight of said polymer in a polymerising zone under polymerising conditions and each resulting portion of mixture is maintained in said zone while said conditions are maintained substantially unchanged for a time sufficient to effect substantial graft polymerization of the monomer or monomers in said composition with said polymer, said composition and polymer being brought together in said manner at constant rates throughout the time in which each portion of mixture is maintained in said zone under said conditions.

16. A process according to claim 15 wherein the graft polymer produced is successively and continuously withdrawn from said zone at a rate correlated to the total rate of addition of said monomer composition and said polymer and such that the mixture in said zone remains substantially unchanged in composition while said monomer composition and said polymer are being brought together and said polymer is being withdrawn.

17. A process according to any of the preceding claims in which composition (2) is substantially completely polymerized and 60% by weight or more of composition (1) is graft polymerized therewith.

18. A process according to claim 17 in which composition (1) is substantially completely graft polymerised.

19. A process for preparing a graft polymer which comprises preparing a graft polymer by a process according to any of the preceding claims and polymerizing with said latter graft polymer present in its polymerization medium more of the chloride monomer or monomers employed in composition (1) sufficient to produce a graft polymer containing from 60% to 95% of said chloride monomer or monomers in a polymerized form.
20. A process according to any of the preceding claims in which the polymerizations are carried out in a dispersing medium in the presence of a polymerisation catalyst.
21. Processes for producing graft polymers substantially as herein described.
22. A graft polymer produced by a process according to any of the preceding claims.
23. A graft polymer formed from vinyl chloride, vinylidene chloride or a mixture of said chlorides and a homopolymer or copolymer of a monomer represented by formulas (a) to (i) as herein defined substantially as herein described.
24. A fibre or film made from a graft polymer claimed in claim 22 or 23.
25. A dyed fibre or film according to claim 24.
26. A solution in an organic solvent of a graft polymer claimed in claim 22 or 23.
- L. E. T. BRANCH, B.Sc., F.R.I.C.,
Patent Agent.